

[54] COUPLING PROCESS
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Related U.S. Application Data

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[52] U.S. Cl. 585/452; 585/453; 585/467
[58] Field of Search 585/452, 453, 467

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[57] ABSTRACT

An alkene selected from ethene, propene, and mixtures thereof is coupled with an aromatic hydrocarbon having an active hydrogen on a saturated alpha-carbon in the presence of a supported potassium or potassium alloy as a catalyst and sodium oxide, potassium oxide, rubidium oxide, or a mixture of any two or all three thereof as a co-catalyst. In preferred embodiments of the invention, the active hydrogen-containing aromatic hydrocarbon is an alkylbenzene, such as toluene; and the co-catalyst is sodium oxide.

15 Claims, No Drawings

COUPLING PROCESS

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending applications Ser. No. 135,318, filed Dec. 21, 1987, now abandoned, and Ser. No. 276,533, filed Nov. 28, 1988 now abandoned.

FIELD OF INVENTION

This invention relates to a process for coupling ethene and/or propene with an aromatic hydrocarbon having an active hydrogen on a saturated alpha-carbon.

BACKGROUND

As disclosed, e.g., in U.S. Pat. Nos. 3,244,758 (Eberhardt), 3,316,315 (Jones), 3,449,455 (Napolitano et al.), and 4,179,580 (Cobb) and in European Patent 128001 (Kudoh et al.), it is known that supported alkali metals, including potassium and sodium-potassium alloys, are useful as catalysts in the coupling of ethylenically-unsaturated hydrocarbons with aromatic hydrocarbons having an active hydrogen on a saturated alpha-carbon. The supported alkali metals are more effective than the corresponding unsupported alkali metals in such reactions but are still not as effective as might be desired.

Claff et al., *Journal of Organic Chemistry*, Vol. 20, pp. 440-442 and 981-986 (1955) disclose the use of sodium oxide in the metalation of toluene by potassium; and the speculative teachings of U.S. Pat. No. 3,691,242 (Cheng et al.) include the substitution of an alkali metal oxide for an alkali metal alkoxide as a co-catalyst in the alkali metal-catalyzed reaction of cumene with ethylene or propylene.

SUMMARY OF INVENTION

An object of this invention is to provide a novel process for coupling ethene and/or propene with an aromatic hydrocarbon having an active hydrogen on a saturated alpha-carbon.

Another object is to provide such a process which utilizes a supported alkali metal as a catalyst.

A further object is to provide such a process in which the reaction rate and product yield are increased.

These and other objects are attained by coupling ethene and/or propene with an aromatic hydrocarbon having an active hydrogen on a saturated alpha-carbon in the presence of a supported potassium or potassium alloy as a catalyst and sodium oxide, potassium oxide, rubidium oxide, or a mixture or any two or all three thereof as a co-catalyst, the catalyst composition containing about 200-1500 weight % of support and about 4-40 mol % of co-catalyst, based on the amount of alkali metal catalyst.

DETAILED DESCRIPTION

As already mentioned, the alkene which is coupled with the aromatic hydrocarbon in the practice of the invention may be ethene, propene, or a mixture thereof. However, it is preferably propene or a propene-ethene mixture.

The aromatic hydrocarbon having an active hydrogen on a saturated alpha-carbon may be any such compound that is known to be useful in such reactions, such as toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, n-butylbenzene, sec-butylbenzene, isobutylbenzene, n-eicosylbenzene, o-, m-, and p-xylenes, o-, m-,

and p-ethyltoluenes, 1,3,5-trimethylbenzene, 1,2,4,5- and 1,2,3,5-tetramethylbenzenes, p-diisopropylbenzene, 1-, and 2-methylnaphthalenes, dimethylnaphthalenes, 1-ethyl-4-n-octadecylnaphthalene, 1,4-di-n-pentynaphthalene, 1,2,3,4-tetrahydronaphthalene, indan, cyclohexylbenzene, methylcyclohexylbenzene, diphenylmethane, etc. However, it is generally a hydrocarbon corresponding to the formula $RR'R''CH$, in which R is an aryl group of up to 20 carbons and R' and R'' are independently selected from hydrogen and alkyl and aryl groups of up to 20 carbons; and it is apt preferably to be an alkylbenzene having one or more ar-alkyl groups. A particularly preferred aromatic hydrocarbon is toluene.

The mol ratio of alkene to aromatic hydrocarbon varies with the particular reactants employed and the products desired, particularly since the aromatic hydrocarbon may have one or more active hydrogens, and it may be desired to react the alkene with only one or with more than one active hydrogen in the aromatic hydrocarbon. It is frequently preferred to employ the reactants in the stoichiometric amounts appropriate for the preparation of the desired product. However, either reactant can be used in excess.

The alkali metal employed as a catalyst may be potassium or a potassium alloy, e.g., a sodium-potassium alloy having a potassium content of 40-90% by weight. As in Cobb, the teachings of which are incorporated herein in toto by reference, it appropriately has its surface area increased by being finely divided or liquid as well as by being supported on any suitable support material which is chemically different from the co-catalyst, such as diatomaceous earth, activated charcoal, granular coke, silica, alumina, pumice, porcelain, quartz, steel turnings, copper shot, sodium carbonate, potassium carbonate, etc. The amount of alkali metal used is a catalytic amount, generally about 2-10 mol %, based on the amount of either of the reactants when they are employed in equimolar amounts or on the amount of the major reactant when they are not utilized in equimolar amounts.

The co-catalyst of the invention is sodium oxide, potassium oxide, rubidium oxide, or a mixture of any two or all three thereof. Like the alkali metal, it is used in finely divided form; and it may be incorporated into the reaction mixture as the oxide, or it may be generated in situ by oxidizing the supported catalyst. It is preferably sodium oxide.

The reaction is conducted by heating a mixture of the alkene, the active hydrogen-containing aromatic hydrocarbon, the supported catalyst, and the co-catalyst under substantially anhydrous conditions at a suitable temperature, generally about 100°-300° C., preferably about 175°-200° C., to couple the reactants. It is generally conducted in the absence of a diluent or in the presence of an excess of the active hydrogen-containing aromatic hydrocarbon as the sole diluent. However, an inert diluent can be used if desired. Exemplary of such diluents are liquid alkanes, cycloalkanes, and aromatic hydrocarbons, such as pentane, hexane, isooctane, cyclohexane, naphthalene, decahydronaphthalene, white oils, etc.

The process of the invention proceeds at a faster rate and provides higher product yields with fewer by-products than comparable processes conducted in the absence of the co-catalyst, and it is particularly advantageous as a means of alkylating alkylaromatic com-

pounds, especially alkylbenzenes, to form compounds useful as solvents, internal standards, intermediates for polymers, pharmaceuticals, or pesticides, etc.

The extent to which the use of both the support and the co-catalyst increases the activity of the potassium or potassium alloy catalyst is surprising. Comparison of experiments in which both the support and the co-catalyst were employed with experiments in which neither was used, experiments in which only the support was utilized, and experiments in which only the co-catalyst was utilized demonstrate that the support and co-catalyst act synergistically to provide an increase in catalytic activity that is greater than the additive effect that might have been expected from the results achieved by the use of the supports and co-catalysts separately.

The following examples are given to illustrate the invention and are not intended as a limitation thereof.

COMPARATIVE EXAMPLE A

A suitable reaction vessel was charged with 92 g (1.0 mol) of toluene, C₁₁ paraffin as a GC standard, and 1.0 g of NaK (an alloy having a K content of 78% by weight). The mixture was stirred and heated to 185° C. in 15 minutes, after which propene was charged until a pressure of 2758 kPa was reached; and the propene pressure was then maintained at 2689-2758 kPa throughout the reaction. Periodically the stirrer was stopped to allow the solids to settle; and samples were drawn, allowed to cool to room temperature, and subjected to GC analysis to determine the amounts of unreacted toluene, desired isobutylbenzene (IBB) product, and n-butylbenzene (NBB), methylindan (MI), and methylpentene (MP) by-products. Finally the reaction was stopped by cooling the reactor to 75° C., venting most of the propene, and injecting 10 mL of methanol under nitrogen pressure to quench the catalyst. The results of the analyses are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
40	100	0	0	0	0
80	91	1.8	0.2	0.01	0.2
160	83	9.6	1.0	0.2	0.9
240	70	17.2	1.6	0.5	1.4

COMPARATIVE EXAMPLE B

Comparative Example A was repeated except that 4.9 g of diatomaceous earth was included in the initial charge to the reaction vessel. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
40	100	0	0	0	0
80	93.0	3.5	0.2	0.46	0.4
120	78.3	11.3	0.53	2.56	1.2
160	66.0	17.4	0.81	4.12	1.7
200	62.1	21.2	0.98	4.90	2.0
240	60.3	22.8	1.05	5.18	2.2

COMPARATIVE EXAMPLE C

Comparative Example A was repeated except that 0.5 g (8.6 mmols) of sodium oxide having a particle size of -325 mesh was included in the initial charge to the

reaction vessel. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
40	—	0.5	0.01	0	0.1
80	95	3.0	0.3	0	0.3
160	78	11.3	1.3	0	0.6
240	72	16.0	1.9	0.11	1.0

EXAMPLE I

Comparative Example A was repeated except that both 4.9 g of diatomaceous earth and 0.5 g of sodium oxide having a particle size of -325 mesh were included in the initial charge to the reaction vessel. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
80	84.9	9.3	1.13	0.13	1.1
120	68.2	25.5	3.22	0.30	2.8
160	48.1	42.5	5.09	0.35	5.5
200	33.3	54.1	6.10	0.38	7.6
240	25.0	61.1	6.45	0.43	9.6

As can be calculated from the % conversions of toluene after 240 minutes in the preceding examples, the activity of the catalyst was increased by 32.3% by using a support in the absence of sodium oxide, decreased by 6.7% by using sodium oxide in the absence of a support, and increased by an amazing 150% by using both the support and the sodium oxide.

EXAMPLE II

Example I was repeated except that the amount of sodium oxide was decreased to 4.3 mmols. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
80	90.2	7.8	0.95	0.13	0.8
120	71.1	23.9	2.95	0.35	2.7
160	50.8	41.0	4.83	0.48	4.9
200	35.8	53.3	5.89	0.56	7.0
240	27.4	60.5	6.30	0.61	8.9

EXAMPLE III

Example II was essentially repeated except that 4.3 mmol of -325 mesh rubidium oxide was substituted for the sodium oxide. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
40	97.5	0.5	0.06	0.01	0.1
80	89.3	6.9	0.77	0.33	0.6
120	77.2	18.7	2.14	0.61	2.0
160	61.3	32.6	3.76	0.84	4.2
200	44.6	47.8	5.43	0.84	5.7
240	37.3	54.1	6.03	0.89	7.2

EXAMPLE IV

Example I was repeated except that the amount of NaK used was 1.3 g. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
80	87.9	11.5	1.44	0.14	0.9
120	65.2	29.4	3.78	0.31	3.0
160	46.5	47.5	5.85	0.35	5.7
200	27.9	60.7	6.96	0.35	8.4
240	18.6	69.0	7.35	0.35	11.5

EXAMPLE V

Example I was repeated except that the sodium oxide employed had a particle size of +80 to -325 mesh. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
80	84.0	9.1	0.94	0.28	0.8
120	66.6	24.7	2.71	0.56	2.2
160	53.4	37.0	3.81	0.67	3.5
200	42.3	45.7	4.46	0.80	4.3
240	36.0	51.4	4.76	0.91	5.2

EXAMPLE VI

Example I was repeated except that the NaK was replaced with 1.0 g of potassium. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
40	99.6	1.7	0.18	0	0.1
80	85.6	11.5	1.48	0.15	1.2
120	63.1	29.0	3.76	0.32	3.1
160	43.4	46.1	5.68	0.36	5.3
200	30.1	57.8	6.61	0.38	7.5
240	21.5	63.4	6.94	0.42	9.2

EXAMPLE VII

Example I was repeated except that the propene pressure was about 2069 kPa. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
120	80.5	18.0	2.29	0.20	1.0
160	64.9	33.4	4.13	0.26	1.8
200	47.6	45.8	5.40	0.31	2.8
240	39.3	52.9	5.89	0.37	3.4

EXAMPLE VIII

Example I was repeated except that the reaction temperature was 165° C. The analytical results are shown below.

Time (min.)	Mols × 100				
	Toluene	IBB	NBB	MI	MP
0	100	0	0	0	0
120	97.7	3.4	0.38	0	0.4
160	93.9	7.4	0.90	0.06	0.9
200	86.2	13.4	1.70	0.14	1.9
240	77.1	20.5	2.63	0.21	2.9

It is obvious that many variations may be made in the products and processes set forth above without departing from the spirit and scope of this invention.

What is claimed is:

1. In a process for coupling an alkene selected from ethene, propene, and mixtures thereof with an aromatic hydrocarbon having an active hydrogen on a saturated α -carbon in the presence of a supported potassium or potassium alloy as a catalyst, the improvement which comprises conducting the reaction in the presence of sodium oxide, potassium oxide, rubidium oxide, or a mixture of any two or all three thereof as a co-catalyst, the catalyst composition containing about 200-1500 weight % of support and about 4-40 mol % of co-catalyst, based on the amount of potassium or potassium alloy catalyst; the support being a material which is chemically different from the co-catalyst.

2. The process of claim 1 wherein the alkene is a mixture of propene and ethene.

3. The process of claim 1 wherein the alkene is propene.

4. The process of claim 1 wherein the aromatic hydrocarbon is a hydrocarbon corresponding to the formula $RR'R''CH$, in which R is an aryl group of up to 20 carbons and R' and R'' are independently selected from hydrogen and alkyl and aryl groups of up to 20 carbons.

5. The process of claim 4 wherein the aromatic hydrocarbon is an alkylbenzene.

6. The process of claim 5 wherein the alkylbenzene is toluene.

7. The process of claim 1 wherein the catalyst is potassium.

8. The process of claim 1 wherein the catalyst is a sodium-potassium alloy having a potassium content of 40-90% by weight.

9. The process of claim 1 wherein the co-catalyst is sodium oxide.

10. The process of claim 1 which is conducted at a temperature of about 100°-300° C.

11. The process of claim 10 wherein the reaction temperature is about 175°-200° C.

12. The process of claim 1 wherein the support is diatomaceous earth.

13. The process of claim 1 wherein the support is potassium carbonate.

14. The process of claim 1 wherein the support is alumina.

15. The process of claim 1 wherein propene is coupled with toluene at about 175°-200° C. in the presence of a supported potassium or sodium-potassium catalyst and sodium oxide as a co-catalyst.

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